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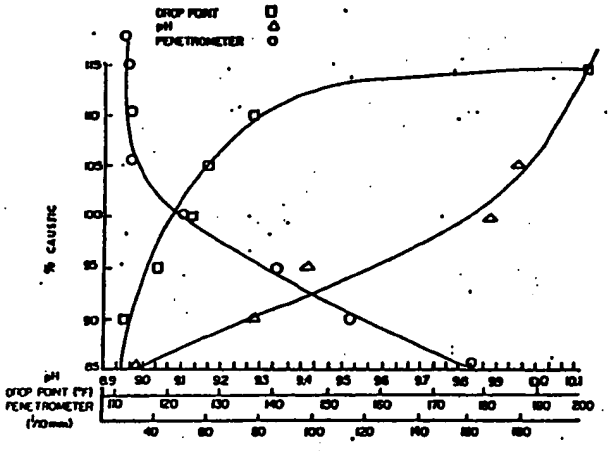
(71) Applicant: DOW CONSUMER PRODUCTS INC.,
9550 Zionsville Road, Indianapolis Indiana 46268 (US)

(72) Inventor: Sabol, John Stephen, Jr., 7462 Harcourt Road,
Indianapolis Indiana 46260 (US)
Inventor: Kester, Wayne Albert, Rr. No. 1 Whitestown,
Indiana 46075 (US)

(74) Representative: Weickmann, Heinrich, Dipl.-Ing. et al,
Patentanwälte Dipl.-Ing. H.Weickmann Dipl.-Phys.Dr.
K.Fincke Dipl.-Ing. F.A.Weickmann Dipl.-Chem. B. Huber
Dr.-Ing. H. Liska Dipl.-Phys.Dr. J. Prechtel
Möhlstrasse 22, D-8000 München 80 (DE)

(54) **Laundry soil and stain remover.**

(57) A prelaundering composition in solid, stick-like form including a surfactant and laundry enzymes homogeneously dispersed throughout a semi-hard carrier vehicle including in-situ formed sodium stearate. Various salts added to the composition of the invention are effective to modify, controllably and independently, particular physical and chemical parameters of the composition, including texture, consistency, hardness, melting point and pH to optimize the rheology and the softening range of the product and to enhance related functional features.



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LAUNDRY SOIL AND STAIN REMOVER

The present invention relates to a solid type fabric-cleaning product which finds utility as a pre--applied spotting agent used prior to a laundering procedure so as to facilitate the removal of stains and soil from selected pre-treated areas of the fabric. More particularly, the invention is directed to a laundry soil and stain removing composition which includes, in combination, surfactants, laundry enzymes, and a carrier material so as to provide a solid medium that can be applied conveniently to a fabric as an aid in laundering. The composition includes a chemical agent for regulating and for selectively, independently modifying physical and chemical parameters of the product to enhance its functional features and its effectiveness in use.

Compositions finding utility as pre-spotting preparations have long been utilized in the laundering and cleaning field. Such preparations have been applied to particular, selected stained or excessively soiled

areas of clothing and other fabrics prior to subjecting the pre-treated material to a laundering operation. It has been established that effective pre-treatment of the type described increases the likelihood of removing the soils and stains effectively.

The specialized preparations of the prior art have taken various physical forms and have embraced a broad variety of chemical formulations. Among such pre-treatment preparations are dry products which have ordinarily been used in conjunction with water to provide a solution in which the fabric to be cleaned is subjected to a pre-soaking step. Other prior products include formulations packaged for spraying from aerosol type dispensers or from bottles fitted with pump mechanisms. Still other specialized preparations constitute preparations which are applied, as liquid pre-spotters, directly to the area to be treated.

Some of the products of the type referred to above have included laundry enzymes of the type which have been demonstrated to act effectively to enhance the removal of foreign material including oil and grease stains and other stains and soil from fabrics. The enzyme systems employed are critically sensitive to the pH of the system into which they are introduced. This fact has interfered with and impaired their use in laundry preparations.

The use of dry powders in conjunction with water is inconvenient, as is the use of liquid pre-spotters.

Aerosol type pre-spotting preparations are costly and suffer the disadvantages inherent in all aerosol type products.

Another shortcoming of prior art "stain sticks" or pre-spotters, particularly those using a sodium stearate matrix, is that it has heretofore not been possible to formulate a product which is soft but which also has a dropping point above 48.9°C a temperature reasonably to be encountered during shipment or warehouse storage.

Many of the products heretofore produced have failed to achieve a balance and functional optimization of the values of interrelated parameters which define and determine the utility and the effectiveness of laundry pre-spotting preparations.

It is also known in the prior art to utilize pre-spotters which take the physical form of stick-like probes or applicators. It is to the improvement of the latter type of product and to the elimination of shortcomings and inadequacies of prior art products that the present invention is directed.

This invention provides a laundry soil and stain remover composition which takes the physical form of an applicator stick with improved physical and chemical properties and which may conveniently be used to apply preferred spot removing and stain removing formulations of the invention to selected areas of fabric, prior to subjecting the fabric to a laundering operation.

It is an important feature of the stain removing compositions of the invention that they include, in combination, a surfactant, and in preferred embodiments, a surfactant system containing both non-ionic and anionic surfactants, one or more laundry enzymes, a bodying agent in which the enzymes and the surfactant are homogeneously distributed, and a chemical agent for selectively and independently modifying the value of one or more physical and chemical parameters of the composition to enhance its operation.

It is a related feature of the invention that the preferred formulations of the invention have proven exceedingly effective to remove stains and soil from cotton fabrics as well as from "synthetics".

Still another very important feature of the invention is the incorporation of a salt into the composition, effectively and selectively to modify a given parameter of the product so as to improve both its physical and its chemical properties and to render the preparation more useful in its intended applications.

A feature of the invention is the discovery that there are critical relationships between the several distinct components of the compositions of the invention and that the concentrations of the components significantly affect the rheology and other properties, including the "dropping point" of the product.

Yet another feature of the invention is that the method of preparing the compositions of the invention includes the step of forming sodium stearate, in-situ, one benefit of this procedure being a significantly reduced cost for raw materials.

It is an important practical advantage of the formulations of the invention that they may be applied as much as several days before subjecting the treated fabric to laundering, with no adverse effects. (The requirement in prior art products that the fabrics so treated must be subjected to washing immediately and the applied pre-spotter not be allowed to dry, has been removed).

In accordance with the present invention the physical properties including the hardness of the final product are effectively controlled by adding a salt to the matrix to control the consistency of the product as well as to maintain the dropping point above 37.8°C, preferably from 48.9°C to 65.6°C. There is provided a simple and highly effective way to raise the dropping point while at the same time decreasing the hardness of the product.

It is an important practical feature of the formulations of the invention that they have been found to function effectively in removing a broad spectrum of stains including milk, blood, ink, cocoa, and sugar, as well as grass soils, on cotton and synthetics.

The formulations of the present invention have the requisite physical strength in combination with the property of being soft enough to be transferred mechanically to the areas to be treated, so that the product may be readily handled and used conveniently, and effectively, and, at the same time, maintaining a physically stable form at the elevated temperatures to which such products are exposed during shipment and storage.

Other and further features, objects, and advantages of the compositions of the invention will be evident from the following description considered in conjunction with the claims and with the accompanying drawing in which Figure 1 is a graphic representation illustrating the inter-relationship between various parameters, including drop point, pH and hardness, of the compositions of the invention.

In preferred embodiments, the aims of the present invention are achieved by formulating a highly effective and versatile cleaning concentrate in the form of a readily manipulable stick-like probe or applicator which includes, in combination, inorganic and organic salts, an enzyme system, a surfactant, the salts, enzymes, and the surfactant being uniformly and homogeneously distributed throughout a supporting matrix or carrier to provide a relatively soft but readily handled rod facilitating the direct application of the composition to selected areas of fabric to be treated. The physical consistency, hardness, softening temperature and the general rheology of the matrix of the product are controlled and adjusted through the addition of the salt or salts.

The compositions of the invention exhibit the requisite values of parameters including adequate rigidity, strength, hardness and temperature sensitivity and stability as well as requisite physical transferability, upon abrasive contact, to the fabric to which the composition is to be applied. Additionally, chemical properties, including the pH, are controlled to ensure an environment in which the enzymes present in the product can perform effectively.

The present invention invokes a unique combination of a system of laundry enzymes in conjunction with, preferably, two or more different types of detergents which augment and supplement one another, all contained as intimately and homogeneously dispersed elements in a carrier medium which includes added salt or salts to provide control over those physical properties and characteristics which ensure stability in shipment and storage and which also make it easy to handle the product physically and to apply the composition of the invention to selected areas which have been delineated for pre-treatment in advance of a laundering operation.

Preferred formulations of the laundry soil and stain remover products of the invention include, as fluid components or solvents in the matrix system, propylene glycol and dipropylene glycol and mixtures of the two. In accordance with the practice of the present invention, the relative ratio and concentrations of the glycols may be selected to alter and define the rheology of the matrix. The dimer produces a harder matrix than does propylene glycol, and the trimer, even harder products. The glycols can be

blended to produce products with desired rheological properties.

In formulations of the type referred to, salts, particularly borate and formate salts (e.g., sodium borate decahydrate) were added for the purpose of enhancing enzyme stability. In the course of this research, the surprising and unexpected discovery was made that these salts and other organic and inorganic salts could be used to control the consistency of the matrix of the product. Upon further research in this area of investigation it was discovered that the value of important parameters, for example, temperature sensitivity, of the products could also be varied and controlled. At the same time, the added salt components could be used effectively to control the pH in the formulated product.

In accordance with the practice of the present invention the addition of the salts is effective not only to raise the drop point and decrease the hardness of the product, but also to increase the hardness, and raise the drop point temperature without raising the pH significantly.

While hardness and drop point may be increased by using more stearic acid and more sodium hydroxide solutions (50% NaOH), the effect is to increase the pH. Such increase is undesirable if there is a pH-sensitive component in the composition. For example, too elevated a pH has an adverse effect on enzyme systems. In the practice of the present invention it is practical, by th addition of a salt, to produce a "harder" formulation without the objectionable side effect of elevating the pH.

In formulations of the type embodied herein, the final product is often translucent to opaque. Accordingly, there may be some difficulty seeing where the product has been applied. The color of the product may also be undesirable or may not be consistent with the color one expects for a laundry product. To correct these features, one can add traditional coloring agents to the formulations. Examples include titanium dioxide, pearlescent agents of the type traditionally used in the cosmetic and soap industry, various organic dyes of the type commonly used in laundry and detergent products, and other coloring and opacifying agents that would impart a color to the product, but which would not dye or discolor the fabric.

The traditional effect the changing of the sodium hydroxide concentration has on pH, hardness (Penetrometer reading), and drop point (temperature response) is shown in Table I and Figure 1. The 100 percent caustic point (Sample D in Table I) represents the formulation listed below (Example 1). The other data represent formulations in which the water/caustic ratio has been changed to give the desired amount of caustic. (See Table I).

TABLE I

SAMPLE #	COMPOSITION	DROP Pt °C	PENETR	pH
A	$[OH^-]$ $[H_2O]$ 21.85 29.65 (15% xs OH^-)	>93.3	29	10.12
B	20.90 30.60 (10% xs OH^-)	58.0	26	10.09
C	19.95 31.55 (5% xs OH^-)	53.5	33	9.96
D	19.00 32.5	51.3	48	9.89
E	18.05 33.45 (5% less OH^-)	48.1	85	9.41
F	17.1 34.40 (10% less OH^-)	44.5	115	9.29
G	16.2 35.35 (15% less OH^-)	45.9	160	8.99

Figure 1 depicts schematically the variations and dependency as well as the inter-relationship between drop point, pH and penetrometer reading as a function of alkali concentration.

Example 1

Ingredient	Conc. (gms)
Propylene Glycol	190.0
Nonylphenol Ethoxylate	75.7
Linear Alcohol Ethoxylate	75.7
Polyethylene glycol	8.0
Dodecylbenzenesulfonic Acid	26.5
Stearic Acid	47.4
Enzyme	25.0

Water/caustic - As shown in Table I

As the graph of Figure 1 indicates, the formulation of Example 1 and other typical sodium stearate

formulations will have very unique properties. The pH, hardness, and drop point are all inter-related and are unique for each given formulation. The drop point of traditional stearate formulations cannot be changed without affecting the other two characteristics.

The present invention provides formulations and a method by which one can change the drop point, for example, and not affect one or both of the other two properties, that is, hardness and pH. The unique utility of the invention is evident upon a consideration of the following additional examples provided for illustrative purposes.

Example 2

The addition of 1 percent sodium chloride to the composition of Example 1 gives a drop point of 54.4°C, a pH of 9.35, and a penetrometer reading of 50. The "comparable" sodium stearate formulation (Example 1) has a drop point of 50.8°C, a pH of 9.36, and a penetrometer reading of 54.

In the salt-modified Example 2 formulation, the drop point has been raised without significantly changing the other characteristics or the values of other input and parameters. In referring to the graph, it will be noted that a sodium stearate formulation with a drop point of 54.4°C would have a pH of 10 and a penetrometer reading of 35. This formulation would be difficult to rub onto the fabric due to its hardness and the pH would be above the optimum for an enzyme, which is generally recognized as being a pH of no high r than 9.5.

Example 3

If one desires a product that is softer, for example, a penetrometer reading of 110, the graph of Figure 1 indicates that the pH of this formulation would be 9.35 and the drop point would be 45°C. The pH of this formulation is within the optimum range for an enzyme, but the dropping point is below the preferred minimum of 48.9°C. The addition of 3 percent sodium borate decahydrate to the formulation, for example, gives the desired product.

Example 4

Another example of the utility of this invention is illustrated with a formulation that would be harder than the formulation illustrated in the previous two examples. If one desires a stick with a penetrometer reading of 38, the graph and Figure 1 indicates that the stearate formulation with that hardness would have a pH of 9.9 and a drop point of 50.6°C. In this example, the dropping point is above the target of 48.9°C, but the pH is above the optimum of 9.5. The addition of 3 percent sodium acetate would give a stick with the desired hardness and pH.

Detergent builders can be added to the prespotter stick formulations. A general class of builders or chelants known as polyaminocarboxylic acids are useful for this function. Examples include sodium nitrilotriacetic acid and hydroxyethyldiaminotriacetic acid. Citric acid and its salts as well as polyacrylic acids can also be utilized for this purpose. The builder is included in the formulations in concentrations from 0.01 to 10 percent.

The utilization of particular salts according to the teachings of this invention is particularly efficacious when builders are incorporated into the formulation. Without the addition of the salts of the invention, the builders have a tendency to crystallize in the matrix. In substituting a more soluble salt of the builder, such as substituting potassium citrate for sodium citrate, the properties of the stick are altered such that the matrix does not have the desired hardness and dropping point. However, the addition of a salt, in accordance with the method of the present invention, will give the desired product.

The products of the invention are waxy, greasy, translucent to opaque solids with a dropping point of, advantageously, 37.8°C to 82.2°C.

A very extensive group of salts can be used in practicing the invention. These salts include the salts of both organic and inorganic acids. Examples are chloride, sulfate, carbonate, phosphate, bromide, formate, acetate, tartrate, borate, and metaborate as the anions, with the cations being sodium, potassium, calcium, lithium, magnesium, and aluminum. This list is meant to be representative and not to exclude other known salts.

Referring now more particularly to the surfactant system, in one preferred embodiment of the invention the surfactants include anionics, in particular, linear alkylbenzene sulfonates, for example, sodium dodecylbenzenesulfonate. These

anionic surfactants function more effectively than do the non-ionics in removing soil and stain from cotton fabrics.

Preferred non-ionic surfactants include ethoxylated linear alcohols, ethoxylated alkylphenols (preferably C_6-C_{12} alkylphenols), and polyethylene glycols.

Within the teachings of the invention, different surfactants may be substituted in the compositions. For example, surfactants of the non-ionic type include ethoxylated linear alcohols, ethoxylated alkylphenols, and polyethylene glycols. Propylene glycol, including the mono, di, and tri anologs, may be used. Various types of stearic acids including single, double and triple pressed stearic acid are suitable. The enzymes used include protease, lipase and amylase, in a stabilized blend, or as unstabilized preparations with calcium salts added for stabilization.

The efficacy and effectiveness of the product has been conclusively demonstrated using test preparations, EMPA-116 (blood, milk, ink), EMPA-112 (cocoa, milk, sugar), and grass soils, on cotton. The swatches were washed in 150 ppm hardness water at 37.8°C, with 100 cycles per minute agitation, and 1.5 g/l non-phosphate powdered commercial detergent (e.g., Tide®).

The test swatches were then read on a Hunter Reflectometer, using the L scale, where L is an indication of lightness-darkness.

PRODUCT	EMPA-112* (STAIN)	EMPA-116* (STAIN)	GRASS* (STAIN)
TIDE®	7.0	28.0	7.1
CLOROX®-2	9.2	56.3	15.5
SHOUT®	13.1	56.2	9.9
PRODUCT OF THE INVENTION	19.2	107.0	15.4

* % Remission = $\frac{\text{Final "L" Reading}}{\text{Initial "L" Reading}}$

The present invention constitutes formulation and methods of controlling the consistency of the solid formulation and the dropping point in spotting sticks. Current art teaches that there is a direct relationship between the dropping point and the hardness of the formulation. That is to say that if one raises the dropping point, the hardness increases. The present invention discloses a technique for raising the dropping point and simultaneously decreasing the hardness of the formulation, an effect which is contrary to what is normally observed in sodium stearate formulations.

	Conc. (parts by weight)	Operational Concentrational Ranges (parts by weight)
Stearic Acid	9.4	5-10
Dodecylbenzene Sulfonic Acid	5.2	3-20
Dipropylene Glycol	3.7	2-6
Propylene Glycol	33.7	20-50
Nonyl Phenol Ethoxylate	14.9	5-30
Linear Alcohol Ethoxylate	14.9	5-30
Polyethylene glycol	1.6	
NAOH-50%	3.7	2-5
Enzyme	5.0	2-10
Sodium Borate Decahydrate	2.9	2-4
Fragrance	0.02	
Water	q.s.	

Example 5

The two surfactants and the glycols are heated to 65.6°C with stirring, until solution takes place. The polyethylene glycol is added next, followed by a water solution containing the sodium borate. When solution has taken place, the sodium hydroxide and sulfonic acid are added. This is followed by addition of the stearic acid. When the stearic acid has dissolved, the temperature is lowered to approximately, 54.4°C, and the enzyme is added with stirring. The resulting formulation is poured into the appropriate mold-like containers or formers.

Products produced in accordance with the invention are characterized by an ASTM penetrometer hardness of 3 to 30 mm using the standard cone with no additional weight added.

CLAIMS.

1. A laundry soil and stain remover composition in applicator stick form including a laundry enzyme, a surfactant, a bodying agent constituting a gelling carrier vehicle for the enzyme and surfactant, the enzyme and surfactant being intimately and uniformly dispersed throughout the carrier to provide a physically self-sustaining solid for direct positive application and material transfer to selected zones of fabrics to be treated, prior to subjecting the fabrics to a laundering cycle, characterized by containing an organic or inorganic salt or a mixture thereof.

2. Composition of Claim 1 characterized in that the salts include at least one chloride, sulfate, carbonate, phosphate, bromide, formate, acetate, tartrate, borate or metaborate, as anions, and sodium, potassium, calcium, lithium, magnesium and aluminum as cations, or mixtures thereof.

3. Composition of Claim 1 or Claim 2 characterized in that the carrier vehicle comprises sodium stearate generated in-situ within the composition.

4. Composition of Claim 1 or Claim 2 characterized in that the composition is a waxy, translucent to opaque solid melting in the range of 40-80°C, and having a hardness in the range of 3 mm to 30 mm measured using an ASTM standard needle with no weight added.

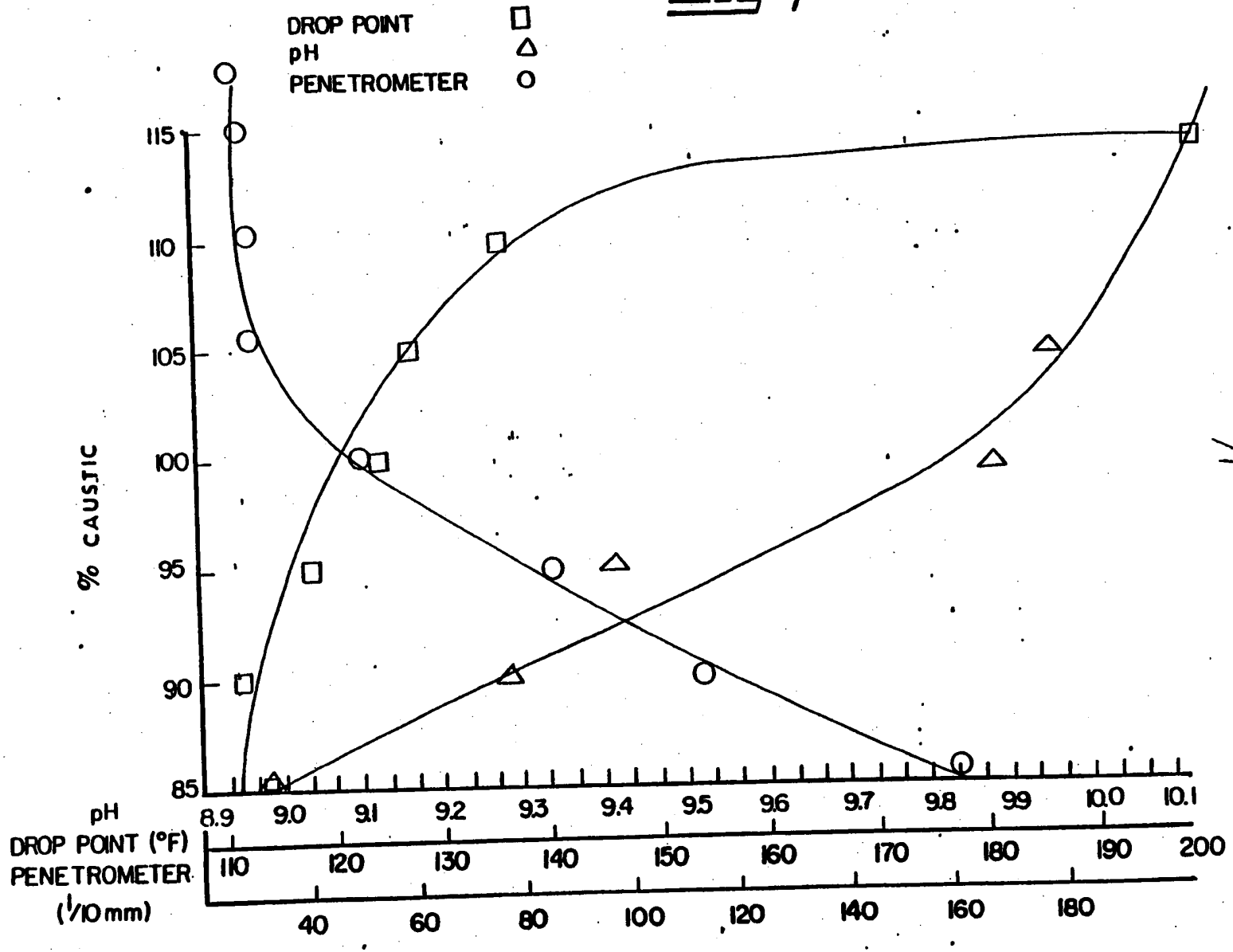
5. Composition of Claim 1 characterized in that the surfactant includes a linear alkyl benzenesulfonate.

6. Composition of Claim 1 characterized in that the surfactant comprises sodium dodecylbenzenesulfonate.

7. Composition of Claim 1 characterized in that the surfactant includes linear alcohol ethoxylates, alkylphenol ethoxylates and polyethylene glycols wherein said carrier vehicle comprises sodium stearate.

8. Composition of Claims 1 or 2 characterized by having a dropping point in the range of 37.8° to 82.2°C.

FIG 1



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(71) Applicant: DOW CONSUMER PRODUCTS INC.,
9550 Zionsville Road, Indianapolis Indiana 46268 (US)

(72) Inventor: Sabol, John Stephen, Jr., 7462 Harcourt Road,
Indianapolis Indiana 46260 (US)
Inventor: Kester, Wayne Albert, Rr. No. 1 Whitestown,
Indiana 46075 (US)

(74) Representative: Weickmann, Heinrich, Dipl.-Ing. et al,
Patentanwälte Dipl.-Ing. H.Weickmann Dipl.-Phys.Dr.
K.Fincke Dipl.-Ing. F.A.Weickmann Dipl.-Chem. B. Huber
Dr.-Ing. H. Liska Dipl.-Phys.Dr. J. Prechtel
Postfach 860820, D-8000 München 86 (DE)

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EUROPEAN SEARCH REPORT

EP 86 10 7435

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 798 181 (VAZQUEZ) * Especially column 5, lines 1-28; column 10, lines 10-18; examples * * Column 5, lines 29-48 *	1,2,4-8 3	C 11 D 3/386 C 11 D 17/00
Y			
Y	US-A-3 953 353 (J.H. BARRETT) * Especially column 4, lines 4-23; claims *	1,3,4,7,8	
P,A	EP-A-0 170 360 (NOVO INDUSTRI) * Claims *	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
C 11 D D 06 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-02-1988	COUCKUYT D.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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